

Support-mediated activation and deactivation of Pt thin films

Valentino R. Cooper, Alexie M. Kolpak, Yashar Yourdshahyan, and Andrew M. Rappe*

The Makineni Theoretical Laboratories,

Department of Chemistry, University of Pennsylvania,

231 S. 34th Street, Philadelphia, PA 19104-6323

(Dated: February 2, 2008)

Abstract

Using ab initio methods, we examine the the charge distribution at the interface of alpha-alumina-supported Pt films, and we consider the influence of this interface on CO adsorption. We demonstrate that a combination of electrostatic charge transfer and covalent bonding governs the interfacial interactions, and that these interactions play an important role in the metal reactivity. By modifying the interface and varying the Pt film thickness over a nanoscale range, CO adsorption can be significantly enhanced or diminished. These observations could be used to tune the reactivity of Pt particles.

INTRODUCTION

The ability to control the interactions of molecules on metal surfaces provides new opportunities for the advance of many technological and industrial processes. Such knowledge will allow for the creation of more efficient catalysts for manufacturing processes, fuel combustion, and the treatment of automotive exhausts and for the production of more sensitive chemical sensors. As a result, the prototypical reaction of CO adsorbing to transition metal surfaces has received much attention. Blyholder used Hückel molecular orbital theory to describe the mechanism by which CO molecules bind to a metal surface [1], thus explaining shifts in CO stretching frequencies for CO binding to various sites. Here, CO binding to the top site on a metal surface involves both the donation of electrons from the filled CO 5σ molecular orbital to the metal d_{z^2} orbitals (direct bonding), and the back-donation of electrons from the metal d_{xz} and d_{yz} orbitals into the CO $2\pi^*$ anti-bonding orbitals. CO binding at metal hollow sites is dominated by back-bonding from the metal d_{xz} and d_{yz} orbitals, with a small contribution from direct bonding to the metal d_{xy} and $d_{x^2-y^2}$ orbitals.

Hammer and Nørskov (HN) later extended this work to illustrate the relationship between the strength of the CO-metal bond and the electronic properties of the metal [2, 3]. Using density functional theory (DFT)[4, 5], they demonstrated that the binding energy of molecules to transition metal surfaces can be correlated to shifts in the centers of the metal d -bands. Since this property could be measured using spectroscopic techniques, their model allowed for the prediction of CO binding strengths using simple surface experiments.

Nanoparticles and thin films further broaden the study of molecule-metal interactions, as nano-dimensional metal particles often exhibit distinctly different properties than bulk. Investigations of gold and platinum nanoparticles indicate that their reactivity is strongly dependent on their size and geometry [6, 7, 8, 9, 10, 11, 12]. In many cases, these particles have enhanced reactivity with decreasing size. Numerous theoretical and experimental studies also suggest that the support material plays an important role in activating or deactivating the surface of metal nanoparticles [10, 13, 14, 15, 16, 17]. Strain studies of metal thin films give evidence that in-plane strain alters the width of the metal d -band and shifts the d -band center toward or away from the Fermi level [18]. In accordance with the HN model, these shifts affect adsorption at the metal surface. Although these studies present clear deviations in the nanosystem as a result of changing the supporting material or the

size or shape of the metal, it is still not clear how the charge boundary at the support-metal interface gives rise to the newly observed properties.

Recent experimental studies by Chen and Goodman of one and two atomic layers of gold supported on TiO_2 show that charge transfer between the support and the metal catalyst have a significant effect on the reactivity at the metal surface [19]. Their thin film geometry eliminated particle shape and support effects to show that the film thickness is a crucial parameter in altering the reactivity at the metal surface.

In this letter, we present DFT calculations to systematically investigate the extent to which the charge distribution at the surface of an α -alumina support alters the electronic properties of Pt thin films. The Pt thin film geometry used in this study excludes particle shape and direct support effects and allows us to concentrate on the effect of the metal-support charge transfer on the metal surface reactivity. We observe dramatic differences in the electronic properties at the metal surface in Pt films of 1-5 atomic layers deposited on oxide supports with different electronegativities, which emphasizes the importance of the underlying substrate. In particular, we show that an electropositive oxide support strengthens the bonding of CO to the metal film, while the electronegative support exhibits non-monotonic bonding to the thin film surface, as a function of layer thickness, resulting in a switch in site preference between a monolayer and a bilayer of Pt. Furthermore, our results demonstrate that the formation of hybrid orbitals at the metal-oxide interface is critical in determining the adsorption properties at the metal surface. We also show that by explicitly considering the symmetry of the metal d -states, particularly of the newly formed hybrid states, the HN model can be extended to describe complex, strongly bound metal-support systems.

METHODOLOGY

We examine a range of metal-oxide interface properties by considering two variations of the α -Alumina surface: the Al-terminated surface (Al_T), which is the most stable clean surface [20], and the strongly polar O-terminated surface (O_T), which is stable when hydrogen or a supported metal is adsorbed [21]. We use a slab geometry with an in-plane $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit cell and periodic boundary conditions to model the alumina surface[22]. The layer stacking can be represented by the formula $(\text{Al-O}_3\text{-Al})_4\text{-Al-O}_3\text{-Al}_m\text{-(Pt}_3)_n$, where

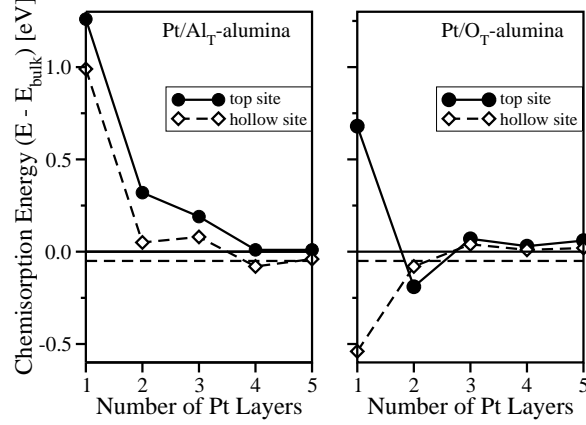


FIG. 1: CO chemisorption energies for the top (●-●) and hollow (◇-◇) sites on the n Pt/Al_T-Al₂O₃ (left) and n Pt/O_T-Al₂O₃ (right) systems. Binding energies are relative to the top site of the Pt(111) surface (—). The (- -) line represents the binding energy of CO at the Pt(111) hollow site.

$m = 0$ or 1 for the O_T and Al_T surfaces, respectively, and n is the number of Pt layers. For both terminations, the interfacial Pt atoms are directly above the surface O atoms, forming a Pt(111) film. All calculations were performed using DFT with the generalized gradient approximation [23] for the exchange correlation functional as implemented in the dacapo code [24], with a planewave cutoff of 30 Ry and a $2 \times 2 \times 1$ Monkhorst-Pack k -point mesh. The theoretical α -Al₂O₃ in-plane lattice constant of 4.798 Å was used (experimental = 4.759 Å [25]). In order to eliminate strain effects, all adsorption energies were compared to unsupported Pt(111) calculations at the same in-plane geometry as the supported metal. (This corresponds to the experimental Pt(111) in-plane lattice constant of 2.77 Å) For our simulations we fixed the ions in the bottom two alumina layers to their theoretical positions, relaxed the third layer perpendicular to the surface, and fully relaxed the remaining alumina layers, Pt layers and adsorbates until the remaining force on each atom was less than 0.01 eV/Å. We correct for known DFT CO chemisorption errors[26, 27] using the extrapolation method of Mason and coworkers [28].

RESULTS

Figure 1 shows the top site chemisorption energy for the adsorption of CO onto the Pt/ α -alumina system as a function of metal layers, relative to Pt(111), on the O_T- and Al_T-

α -alumina surfaces. For both terminations, the first layer of Pt ions are deposited above alumina surface oxygen ions. In both cases, a monolayer of metal on the surface results in an enhancement of the CO top site binding energy relative to Pt(111). For Pt on the Al_T surface, a monotonic decrease in the chemisorption energy is observed as the Pt film thickness is increased. The system returns to Pt(111) behavior at four layers of Pt. In contrast, the adsorption of CO on the Pt/ O_T system is non-monotonic. In this case, there is a dramatic decrease in the top site chemisorption energy and an increase in the hollow site chemisorption energy for two layers of Pt, such that the binding of CO to the surface is weaker than for Pt(111). For three layers of Pt on the O_T surface, the chemisorption energy oscillates above the Pt(111) energy, eventually returning to the Pt(111) value for $n > 4$.

Table I tabulates the site preference energy ($E_{\text{top}} - E_{\text{fcc}}$) for CO adsorption on the Pt/alumina system as a function of metal layers. Here we see that both the Pt/ Al_T - and the Pt/ O_T -alumina monolayer systems show a stronger preference for top site binding than the bulk material. However, the Pt/ O_T system shows a much larger preference toward top site binding than the Pt/ Al_T system. Furthermore, the Pt/ Al_T system binding energies asymptote to that of Pt(111) with increasing film thickness, while the Pt/ O_T bilayer exhibits a switch in site preference. Table I also indicates a much greater effect on the site preference energy, as thicker films ($n > 5$) are needed before the Pt/ O_T system fully returns to Pt(111).

No. Pt Layers	Al_T Site	O_T Site	Al_T Term. (eV)			O_T Term. (eV)		
	Pref.	Pref.	d_{z^2}	d_{xy}	d_{xz}	d_{z^2}	d_{xy}	d_{xz}
1	0.27	1.22	0.49	0.54	0.55	0.36	-0.23	-0.78
2	0.27	-0.11	-0.04	0.09	0.05	0.14	0.00	-0.07
3	0.11	0.03	-0.10	0.02	0.03	-0.06	0.01	0.03
4	0.09	0.02	0.01	0.00	-0.01	0.03	0.01	0.03
5	0.05	0.04	0.00	0.00	0.00	0.00	0.00	-0.01
Pt(111)	0.05	0.05	-1.35	-2.03	-1.64	-1.35	-2.03	-1.64

TABLE I: CO site preference energy, $E_{\text{top}} - E_{\text{fcc}}$, and shifts in the d - band centers relative to Pt(111) for the $n\text{Pt}/\text{Al}_2\text{O}_3$ system. All energies are in eV.

DISCUSSION

When a transition metal is deposited onto a support material, the metal d -states change as the metal interacts with the substrate. According to the HN model, upward or downward shifts in the metal d -band center can cause corresponding increases or decreases in the bonding interaction of molecules with the metal surface. To apply the HN model to describe the Pt/Al₂O₃ systems, we decompose the metal d -band and consider the shifts of the individual d -orbitals. These are summarized in Table 1.

When a single layer of Pt is deposited on the Al_T surface, the electropositive Al ions donate charge to the surface metal atoms. This transfer of electrons results in an upward shift in the metal d -band center, relative to Pt(111). We can decompose the d -bands of the metal surface atoms to consider the orbitals involved in CO bonding. In Table I we see that there is a large upward shift (0.55 eV) in the d_{xz} and d_{yz} band centers relative to Pt(111), as can be seen in the large increase in the area under the peak just below the Fermi level. This shift makes more states of appropriate energy available for back donation to the CO $2\pi^*$ orbital, greatly enhancing the binding at the top and hollow sites. While such a large increase in back-bonding might suggest a more pronounced enhancement of hollow site binding energy (and thus a decrease in the site preference energy), this is not the case because of the nature of the direct bonding at the top and hollow sites. The number of free states in the d_{z^2} orbitals (Figure 2A) is similar to that in Pt(111), resulting in negligible changes in the direct bonding contribution to the top site binding energy. On the other hand, interaction of the d_{xy} and $d_{x^2-y^2}$ orbitals with the surface Al atom results in a large upwards shift in these states, reducing the number of free states near the Fermi level accessible for receiving electrons from the CO 5σ (Figure 2B). This loss in free states, combined with the small spatial overlap between these orbitals and the CO 5σ , significantly decreases the direct-bonding contribution at the hollow site. Consequently, there is a much larger top site preference for this system compared to unsupported Pt(111) (Figure I).

The bilayer of Pt metal shows a shift of all of the metal d -orbitals (Figure 2A-C) back towards their Pt(111) arrangement. The d_{xz} and d_{yz} are still shifted up by 0.05 eV relative to Pt(111) (Table I), exhibiting stronger back-bonding. Furthermore, there are more free d_{z^2} states than Pt(111) available for direct-bonding, while there is a decrease in the number of free d_{xy} and $d_{x^2-y^2}$ orbitals relative to Pt(111). This again causes there to be a stronger

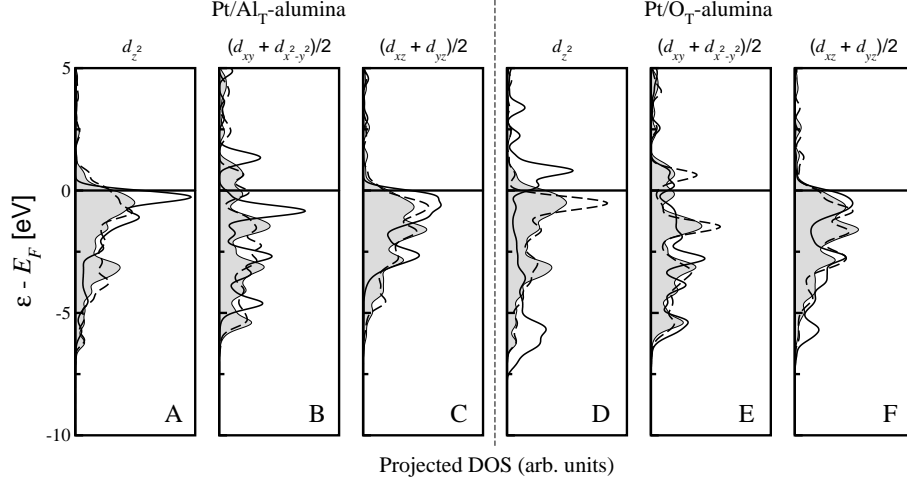


FIG. 2: The density of states (DOS) plots for the surface Pt atoms for the Pt/ α -alumina system. (A-C) are projected DOS for the Pt/ Al_T system and (D-F) are projected DOS for the Pt/ O_T system. (A) and (D) depict the DOS projected onto the d_{z^2} orbitals, (B) and (E) are the average of the DOS projected onto the d_{xy} and $d_{x^2-y^2}$ orbitals, and (C) and (F) are the average of the DOS projected onto the d_{xz} and d_{yz} orbitals for each system. The shaded regions represent the Pt(111) surface, the solid (—) lines are for the monolayer and the dashed (---) lines are for the bilayer.

preference towards top site binding (Figure I). For three or more layers of Pt, the DOS of the surface atoms returns to the Pt(111) value, as do the top and hollow site chemisorption energies.

Figure 1 shows that for a single layer of Pt on the O_T surface there is an increase in CO top site binding strength by 0.69 eV relative to Pt(111). However, an analysis of the DOS for the one layer Pt/ O_T system shows that the d -band center shifts down by 0.60 eV relative to Pt(111). These results can not be described by the basic HN model bonding picture, which would predict a decrease in the chemisorption energy. To understand the origin of this difference, we need to consider the bonding at the metal-oxide interface and its effect on the surface metal d -states.

When a platinum atom is deposited onto the O_T -alumina surface, there is a transfer of electrons from the platinum atoms to the more electronegative oxygen atoms. More importantly, this interaction results in the formation of hybrid orbitals between the Pt metal and the oxide surface atoms. Figures 2 D-F show the projected DOS for the top layer Pt metal d -orbitals as a function of layer thickness. Here we see, for the monolayer, the

creation of hybrid orbitals causes a splitting of both the d_{z^2} (Figure 2D) and the d_{xz} and d_{yz} (Figure 2F) orbitals. The downshift in the d -band center is related to the large splitting of the d -orbitals into these hybrid orbitals, creating a higher energy anti-bonding orbital and a much lower energy bonding orbital. The new d_{z^2} anti-bonding orbital has the correct symmetry for bonding with the CO 5σ orbital and has a much greater number of free states available to accept electrons from the CO molecule. This strengthens the direct bonding between the CO molecule and the metal surface and explains the large increase in the CO top site chemisorption energy. Hollow site bonding, on the other hand, is more affected by changes in the remaining d -orbitals. The overall downward shift in d_{xz} and d_{yz} band centers (Table I) reduces the amount of electrons of suitable energy available for back-donation. Simultaneously, there is a reduction in the number of free d_{xy} and $d_{x^2-y^2}$ orbitals, further inhibiting the direct binding at the hollow site. These effects are manifested in the huge site preference for the single layer Pt/ O_T system.

For the bilayer of Pt on O_T -alumina, we see that there is still a downward shift of the d -band center relative to Pt(111), corresponding to the observed decrease in top site chemisorption energy. In this case, the top layer is not directly in contact with the oxide support, and no hybrid orbitals are formed. However, the surface Pt atoms interact with the hybrid orbitals of the interfacial Pt atoms, resulting in a shift of their d_{z^2} orbitals below the Fermi level (Figure 2D). The dramatic reduction in free d_{z^2} states causes a decrease in the top site binding energy relative to Pt(111). On the other hand, the d_{xz} and d_{yz} (Figure 2F) orbitals now resemble Pt(111) states, restoring most of the bulk back-bonding character. Additional shifts in the d_{xy} and $d_{x^2-y^2}$ orbitals at the Fermi level reduces the direct bonding at the hollow site (similar to the 1LPt/ Al_T case); therefore the hollow site binding energy is slightly less than observed for Pt(111). The large weakening of top site binding and the small difference in hollow site binding result in a change in the site preference of Pt/ O_T bilayers. Similar to Pt/ Al_T , both the chemisorption and site preference energies begin to return to Pt(111) values for thicker films as the top layer DOS begins to resemble that of Pt(111). Due to the larger charge transfer at the Pt/ O_T interface, and the formation of hybrid orbitals within the first layer of Pt, there is less charge screening in the Pt thin film, causing a slower return to Pt(111) values for $n > 5$.

CONCLUSION

In conclusion, we have shown how changes in the charge distribution at the metal-support interface affect adsorption of CO on the surface of Pt metal thin films. Our results present a theoretical basis for beginning to understand the interactions between an oxide support and the properties at the metal surface. Using a modified HN model, we show that the changes in the metal surface properties can be correlated to the changes in the electronic properties of the metal d -states as they interact with the oxide support. While it is known that low-coordinated sites greatly enhance the reactivity of metal particles [7, 8], these results demonstrate the importance of metal-support charge transfer in defining the properties at the metal surface, offering further support for the recent work of Chen and Goodman. In addition, our findings suggest that increased reactivity at the perimeter of metal particles with diameters < 5 nm [10, 11, 17, 29] may be partially attributed to the strong metal-oxide coupling accessible at these boundaries.

The very different CO adsorption behavior as a function of Pt film thickness for the two surface terminations shows that coupling between the metal and oxide support is also sensitive to the surface polarization of the oxide. The fact that these results are greatly diminished at four or five layers indicates that this is a nanoscale effect. Our study demonstrates the wide range of chemical activity that can be accessed by manipulating the oxide support and the thickness of the metal film, offering numerous possibilities for the design of more reactive/selective catalysts for applications as diverse as chemical sensors, fuel cells, and photochemical reactions.

ACKNOWLEDGMENTS

We thank Sara E. Mason and Ilya Grinberg for discussions on CO adsorption energy corrections. This work was supported by the Air Force Office of Scientific Research, under Grant No. FA9550-04-1-0077, and the Office of Naval Research, under Grant No. N-000014-00-1-0372. Computational support was provided by the High-Performance Computing Modernization Office of the Department of Defense and the Defense University Research Instrumentation Program. A.M.R. thanks the Camille and Henry Dreyfus Foundation for support. V.R.C. thanks IBM and ACS for support through the IBM Graduate Student

Award in Computational Chemistry. A.M.K. was supported by a GAANN fellowship.

* Electronic address: rappe@sas.upenn.edu

- [1] G. Blyholder, J. Phys. Chem. **68**, 2772 (1964).
- [2] B. Hammer and J. K. Norskov, Surf. Sci. **343**, 211 (1995).
- [3] B. Hammer, Y. Morikawa, and J. K. Norskov, Phys. Rev. Lett. **76**, 2141 (1996).
- [4] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [5] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [6] G. Mills, M. Gordon, and H. Metiu, Chem. Phys. Lett. **359**, 493 (2002).
- [7] Z. L. Wang, T. S. Ahmad, and M. A. El-Sayed, Surf. Sci. **380**, 302 (1997).
- [8] J. W. Yoo, D. J. Hatcock, and M. A. El-Sayed, J. Cat. **214**, 1 (2003).
- [9] B. Yoon, H. Hakkinen, and U. Landman, J. Phys. Chem. A **107**, 4066 (2003).
- [10] M. Haruta, Catal. Today **36**, 153 (1997).
- [11] M. Valden, X. Lai, and D. W. Goodman, Science **281**, 1647 (1998).
- [12] A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Hakkinen, R. N. Barnett, and U. Landman, J. Phys. Chem. A **103**, 9573 (1999).
- [13] C. Bozo, N. Guilhaume, and J.-M. Herrmann, J. Catal. **393**, 393 (2001).
- [14] E. J. Walter, S. P. Lewis, and A. M. Rappe, Surf. Sci. **495**, 44 (2001).
- [15] L. M. Molina and B. Hammer, Phys. Rev. Lett. **90**, 206102 (2003).
- [16] R. Lindsay, E. Michelangeli, B. G. Daniels, M. Polick, A. Verdini, L. Floreano, A. Morgante, J. Muscat, N. M. Harrison, and G. Thornton, Surf. Sci. **547**, L859 (2003).
- [17] E. S. Putna, J. M. Vohs, and R. J. Gorte, Surf. Sci. Lett. **391**, L1178 (1997).
- [18] M. Mavrikakis, B. Hammer, and J. K. Norskov, Phys. Rev. Lett. **81**, 2819 (1998).
- [19] M. S. Chen and D. W. Goodman, Science **306**, 252 (2004).
- [20] J. Toofan and P. R. Watson, Surface Science **401**, 162 (1998).
- [21] P. J. Eng, T. P. Trainor, G. E. B. Jr., G. A. Waychunas, M. Newville, S. R. Sutton, and M. L. Rivers, Science **288**, 1029 (2000).
- [22] L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. **47**, 781 (1925).
- [23] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Physical Review B **46**, 6671 (1992).

- [24] B. Hammer, L. B. Hansen, and J. K. Norskov, Phys. Rev. B **59**, 7413 (1999).
- [25] W. E. Lee and K. P. D. Lagerlof, J. Electron Microsc. Techn. **2**, 247 (1985).
- [26] P. J. Feibelman, B. Hammer, J. K. Norskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic, J. Phys. Chem. B **105**, 4018 (2001).
- [27] I. Grinberg, Y. Yourdshahyan, and A. M. Rappe, J. Chem. Phys. **117**, 2264 (2002).
- [28] S. E. Mason, I. Grinberg, and A. M. Rappe, Phys. Rev. B **69**, 161401(R) (2004).
- [29] U. Heiz, S. Abbet, A. Sanchez, and W. D. Schneider, J. Am. Chem. Soc. **121**, 3214 (1999).